Accepted Manuscript

Experimental and theoretical studies of (FT–IR, FT–Raman, UV–Visible and DFT) 4-(6-methoxynaphthalen-2-yl) butan-2-one

P. Govindasamy, S. Gunasekaran

PII:	S1386-1425(15)00515-6
DOI:	http://dx.doi.org/10.1016/j.saa.2015.04.043
Reference:	SAA 13594
To appear in:	Spectrochimica Acta Part A: Molecular and Biomo- lecular Spectroscopy
Received Date:	30 November 2014
Revised Date:	1 April 2015
Accepted Date:	16 April 2015



Please cite this article as: P. Govindasamy, S. Gunasekaran, Experimental and theoretical studies of (FT–IR, FT–Raman, UV–Visible and DFT) 4-(6-methoxynaphthalen-2-yl) butan-2-one, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2015), doi: http://dx.doi.org/10.1016/j.saa.2015.04.043

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Submissions Needing Revision

Experimental and theoretical studies of (FT–IR, FT–Raman, UV–Visible and DFT) 4-(6methoxynaphthalen-2-yl) butan-2-one

P. Govindasamy^{a,*} S. Gunasekaran^{a,b}

^aDepartment of Physics, Karpagam University, Eachanari, Coimbatore-641021, TN, India.

^bDean, Research and Development St.Peter's Institute of higher education and research,

St. Peter's University, Avadi, Chennai – 600054, TN, India.

*Corresponding Author (Email: pgovindasamy1985@gmail.com)

Tel.: +91 9976735346

Abstract

In this work, the vibrational spectral analysis was carried out by using FT–Raman and FT–IR spectroscopy in the range 4000–50 cm⁻¹ and 4000–450 cm⁻¹ respectively for 4-(6-methoxynaphthalen-2-yl) butan-2-one (abbreviated as 4MNBO) molecule. Theoretical calculations were performed by Density Functional Theory (DFT/B3LYP) method using 6–311G(d,p) and 6–311++G(d,p) basis sets. The difference between the observed and calculated wavenumber value of most of the fundamentals were very small. The complete vibrational assignments of wavenumbers were made on the basis of potential energy distribution (PED). The UV–Vis spectrum was recorded in the methanol solution. The energy, wavelength and oscillator's strength were calculated by Time Dependent Density Functional Theory (TD–DFT) and matched to the experimental findings. The intramolecular contacts have been interpreted using Natural Bond Orbital (NBO) and Natural Localized Molecular Orbital (NLMO) analysis. Thermodynamic properties of 4MNBO at different temperature have been calculated. The molecular electrostatic potential surface (MESP) and Frontier molecular orbital's (FMO's) analysis were investigated using theoretical calculations.

Keywords: 4MNBO, FT-IR, FT-Raman, NBO, MESP.

1. Introduction

4MNBO, a nonsteroidal anti-inflammatory drug (NSAID) of the arylalkanoic acid family (which includes diclofenac). It contains a naphthalene moiety, which consists of two fused benzene rings. It is widely used for the treatment of pain, osteoarthritis, rheumatoid arthritis, fever, swelling, inflammation and platelet aggregation. The 4MNBO and its derivatives were studied by several authors. Basha et al, studied High Performance Liquid chromatography (HPLC) with UV detection [1], fluorometric detection [2], Liquid Chromatography Mass Spectrometry (LC–MS) [3], gas chromatographic [4], High Performance Thin Layer Chromatographic (HPTLC) [5], colorimetric [6], liquid chromatographic [7] and High Performance Liquid Chromatographic (HPLC) [8]. Some reports could be found in the scientific literature for the spectrophotometric determination of 4MNBO in pharmaceutical preparations. The analytical techniques include micellar electrokinetic chromatographic [9], electro analytical methods [10] and flow injection analysis [11]. Few phosphorimetric methods were carried out for the evaluation of 4MNBO in pharmaceuticals [12] in addition to some electochemical techniques such as cyclic, differential pulse and square wave voltammetric techniques [13].

Literature survey reveals that to the best of our knowledge, DFT frequency calculations of the title compound 4MNBO have not been reported so far. In our present investigations, the FT–IR and FT–Raman vibrational wavenumbers were observed and the wavenumbers were theoretically calculated by using quantum chemical calculations. It must be mentioned that this was the first time that a detailed theoretical analysis was carried out on the spectroscopic properties of 4MNBO. Density functional theory (B3LYP/6–311G(d,p) and B3LYP/6–311++G(d,p)) calculations have been performed to support our wavenumber assignments. The Natural Bond Orbital (NBO) and Natural Localized Molecular Orbital (NLMO) analysis which explains the most important orbital interactions in order to classify general structure features. The Natural charge analysis, wavelength, oscillator strength and energy have also been calculated. The electronic properties, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the compound were computed. A visual representation of the chemically active sites and comparative reactivity of atoms have been obtained by mapping electron density isosurface with electrostatic potential. The temperature dependence of thermodynamic properties was analyzed.

2. Experimental

The powder form of 4MNBO was procured from leading pharmaceutical company Sigma Aldrich in Chennai and used as such without further purification. The FT–IR spectrum of powder 4MNBO was recorded in the range 4000–450 cm⁻¹ on Bruker IFS 66V spectrometer using KBr pellet technique with 4.0 cm⁻¹ resolution. The FT–Raman spectrum recorded using 1064(nm) line of Nd:YAG laser as excitation wavelength in the 4000–50 cm⁻¹ region on Bruker IFS 66V spectrometer with FRA 106 Raman module which was used as an accessory. The UV-Visible spectral measurements were carried out in methanol solution using a Varian Cary 5E UV–NIR spectrometer. The spectral measurements were carried out at Sophisticated Analysis Instrumentation Facility (SAIF), IIT Madras–India.

3. Computational details

The entire quantum chemical calculations were performed at DFT/B3LYP level with 6-311G(d,p) and 6-311++G(d,p) basis sets to predict the molecular structure and vibrational wavenumbers using the Gaussian 09 W program [14]. The B3LYP represents Becke's three parameter hybrid functional method [15] with Lee–Yang–Parr's correlation functional (LYP) [16]. The assignments of the calculated wavenumbers were aided by GAUSSVIEW 5.0 program, which gives a visual presentation of the vibrational modes [17]. The potential energy distribution (PED) was calculated with the help of VEDA 4 program package [18]. The Natural bond orbital (NBO) and Natural Localized Molecular Orbital (NLMO) analysis calculations were performed. The absorption wavelengths, energies and oscillator strengths were calculated using B3LYP method of the TD-DFT, based on the optimized structure in solution and gas phase. Moreover, the changes in the thermodynamic functions (the heat capacity, entropy, and enthalpy) were investigated for the different temperatures from the vibrational frequency calculations of the title molecule. Additionally, HOMO, LUMO energy values and energy gap for 4MNBO were calculated by using B3LYP method with 6-311G(d,p) and 6-311++G(d,p) basis sets. Furthermore, molecular electrostatic potential (MESP) were plotted in 3D by using optimized structures at B3LYP with 6-311++G(d,p) basis set.

4.0 Result and discussion

4.1 Molecular geometry

The optimized geometry of 4MNBO was shown in Fig. 1 and the corresponding structural parameters of bond length and bond angle values were shown in Table 1. The optimized structural parameters of 4MNBO were determined at the DFT/B3LYP and 6-311G(d,p) and 6-311++G(d,p) basis sets. From the theoretical values, it was found that some of the calculated parameters were slightly deviated from the experimental values, due to fact that the theoretical calculations belong to molecule in the gaseous phase and the experimental results belong to molecule in the solid state. The experimental data on the geometrical structure of the related molecule was compared with the theoretical values [19]. The bond length of C_{12} - C_{13} for B3LYP method with 6–311G(d,p) basis set was 1.4173Å but B3LYP with 6–311++G(d,p) basis set 1.4171Å which was closer to the experimental data (1.4162Å). The` average bond distances of C-C in the benzene ring calculated by B3LYP method with 6-311++G(d,p) basis set was 1.4043Å. The bond lengths of C–C bond changes in value, which was due to the substitutions on the benzene ring in the place of hydrogen atom. The optimized C₁₄-C₁₅ bond length were calculated 1.4149Å by B3LYP with 6-311++G(d,p) and 1.4146Å by B3LYP with 6-311G(d,p)basis set. By comparing those values with the experimental value of 1.1461Å, it was observed that B3LYP/6–311++G(d,p) estimate the C_{14} – C_{15} bond length better than B3LYP/6–311G(d,p) method. The optimized C_1 - C_2 bond length were 1.5188 and 1.5177Å for B3LYP method with 6– 311G(d,p) and 6-311++G(d,p) basis sets respectively. The observed C_2-O_5 , $C_{12}-O_{16}$ and $O_{16}-O_{16}$ C₁₇ bond length values were found to be 1.2030, 1.3611 and 1.4190Å and the calculated bond length values were 1.2121, 1.3675 and 1.4209Å by B3LYP method using 6-311++G(d,p) basis set.

Furthermore, $C_1-C_2-C_3$ bond angle in the structure were observed at 116.2500° this angle value were calculated at 116.2757° by B3LYP with 6–311++G (d,p) basis set. The experimental $C_1-C_2-O_5$, $C_6-C_{15}-C_{10}$ and $C_3-C_2-O_5$ bond angles were found at 121.5300, 119.3600 and 122.2100° and these angles were calculated at 121.5908, 119.2898 and 122.1326° by B3LYP with 6–311++G (d,p) basis set.

4.2 Vibrational analysis

The title molecule 4MNBO has C₁ point group symmetry and has 33 atoms, which possess 93 normal modes of vibrations. The harmonic-vibrational frequencies were calculated and compared with the experimental frequencies. It was given in Table 2. The experimental and simulated FT-IR and FT-Raman spectra were shown in Figs. 2 and 3, respectively. The calculated wavenumbers were slightly higher than the observed values for the majority of the normal modes. Two factors may be responsible for the discrepancy between the experimental and computed spectra of this compound. The first reason was due to the environment and the second reason was due to the fact that the experimental value is an anharmonic wavenumber while the calculated value was a harmonic wavenumber. The observed slight disagreement between theory and experimental could be noted that the calculations were made for a free molecule in vacuum, while experiments were performed for solid samples. Furthermore, the anharmonicity was neglected in the real system for the calculated vibrations. Therefore, it was customary to scale down the calculated harmonic wavenumber in order to improve the agreement with the experimental values. After applying a uniform scaling factor, the theoretical calculation reproduces the experimental data well. The harmonic frequencies were calculated by B3LYP method using 6-311G(d,p) and 6-311++G(d,p) basis sets and then scaled by 0.9655 and 0.9650 respectively. The experimentally observed and theoretically calculated harmonic vibrational frequencies and their correlations were gathered in Table 2. The vibrational bands assignments were made by using the PED analysis and the animation option of Gauss View 5.0 graphical interface for Gaussian. The maximum number of values determined by B3LYP/6-311++G(d,p) method was in fairly agreement with the experimental values and was also confirmed by the scale factors used to get the scaled frequencies.

C–H Vibrations

The aromatic compounds absorb in the region 3100–3000 cm⁻¹ due to ring C–H stretching vibrations [20-21]. In our present work, the bands were observed at 3096 and 3079 cm⁻¹ in FT–Raman and 3057 cm⁻¹ in FT–IR were assigned to the C–H stretching vibrations of the title compound.

The calculated scaled frequency at 3091, 3072, 3061 and 3091, 3071, 3060 cm⁻¹ by B3LYP method with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively were presented in Table 2. The C–H in-plane bending vibrations occur in the region 1475–1450 cm⁻¹. The band observed at 1466 and 1452 cm⁻¹ in FT–IR and 1457 cm⁻¹ in FT–Raman were assigned to C–H in-plane bending vibrations. The calculated scaled wavenumber values of the mentioned mode were found at 1467, 1453 and 1463, 1452 cm⁻¹ by B3LYP method with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively were presented in Table 2. The C–H torsion vibrations were observed at 1262, 932, 894, 844 and 694 cm⁻¹ in FT–IR and 1271, 894, 865, 832 and 695 cm⁻¹ in FT–Raman. The theoretically calculated scaled values were 1269, 939, 907, 873, 849, 714 and 1269, 941, 909 870, 849, 714 cm⁻¹ by B3LYP level with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively. These scaled wavenumbers were in fairly agreement with the experimental values.

CH₂ and CH₃ Vibrations

Methylene group stretching vibrations occur in the region near 2926 cm⁻¹. The position of these bands does not vary more than ± 10 cm⁻¹ in the aliphatic and nonstrained cyclic hydrocarbons [22]. The frequency of the methylene stretching is increased when the methylene group is part of a strained ring. The present case CH₂ stretching vibrations have been observed at 2936 cm⁻¹ in FT–IR and 2932 cm⁻¹ in FT–Raman were assigned to CH₂ stretching vibrations. The calculated wavenumbers of this mode was 2940 and 2938 cm⁻¹ in B3LYP level with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively were presented in Table 2. The C–H stretching in CH₃ occurs at lower frequencies than those of aromatic ring. For CH₃ compound the mode appear in the region 2962–2872 cm⁻¹[23, 24]. In the present work, the FT–IR bands observed at 2896 cm⁻¹ and the FT–Raman bands observed at 2895 cm⁻¹ have been assigned to CH₃ stretching vibrations. The theoretically calculated scaled values were 2895 and 2898 cm⁻¹ by B3LYP method with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively were presented in Table 2.

C=O and C-O Vibrations

Generally the C=O occur in the region $1720-1700 \text{ cm}^{-1}$ [25]. In the present study, the very strong bands observed at 1705 cm⁻¹ in FT-IR and a very weak band obtained at 1704 cm⁻¹ in FT-Raman were assigned to C=O stretching vibrations. The theoretically calculated scaled values by B3LYP method 6-311G(d,p) and 6-311++G(d,p) basis sets at 1722 and 1718 cm⁻¹ were assigned to C=O stretching vibration in fairly agreement with the experimental FT-IR and FT-Raman spectra. The C-O stretching vibrations are appearing in the range of 1300-1000 cm⁻ ¹[24]. In the FT–IR spectrum, the very strong band observed at 1027 cm⁻¹ was assigned to C–O stretching vibrations. The corresponding very weak Raman pecks was observed at 1029 cm⁻¹ respectively. The theoretical scaled wavenumbers of C-O stretching vibrations were at 1030, 1028 and 1026, 1028 cm⁻¹ by B3LYP methods with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively. The C–O in-plane bending vibrations were found at 574 and 507 cm⁻¹ in FT–IR and 576, 508, 362, 274 and 182 cm⁻¹ in FT-Raman for 4MNBO. The calculated bands found at 564, 506, 358, 276 and 181 cm⁻¹ in B3LYP/6-311G(d,p) and 561, 505, 357, 276 and 180 cm⁻¹ in B3LYP/6–311++G(d,p) methods respectively. In the FT-IR spectrum, the weak band observed at 564 cm⁻¹ was assigned to C–O out-of-plane bending vibration. The corresponding very weak Raman pecks were observed at 433 and 207 cm⁻¹ respectively. The C–O torsion vibration was found at 103 cm⁻¹ in FT–Raman spectrum.

C=C and **C-C** Vibrations

The C=C aromatic stretching vibrations give rise to characteristic bonds in both the observed FT-IR and FT-Raman spectra, covering the spectral region ranging from 1650–1430 cm⁻¹ [26]. In our study the C=C stretching vibrations of the present compound observed at 1610 cm⁻¹ in FT-IR and 1575 cm⁻¹ in FT-Raman were assigned to C=C stretching vibrations respectively. The calculated scaled values were 1617, 1593 and 1614, 1589 cm⁻¹ by B3LYP methods with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively. The ring C-C stretching vibrations normally occur in the region 1590–1430 cm⁻¹ [27]. The present case C-C stretching vibrations have been observed at 1484 cm⁻¹ in FT-IR and the band observed at 1485 cm⁻¹ in FT-Raman were due to C-C stretching vibrations. These vibrations were identified with the PED values.

The calculated wavenumbers at 1488 and 1485 cm⁻¹ by B3LYP methods with 6– 311G(d,p) and 6–311++G(d,p) basis sets respectively. The C–C stretching vibrations predicted by B3LYP with 6–311++G(d,p) basis set value was in fairly agreement with the experimental values as presented in Table 2. The bands were observed at 798, 736, 660, 610, and 525 cm⁻¹ in FT–IR and 795, 613, 525,429, 401, 274 and 103 cm⁻¹ in FT–Raman have been assigned to C–C in plane bending vibrations. The C–C out-of-plane bending vibrations were found at 564 and 472 cm⁻¹ in FT–IR. The C–C torsion vibrations were observed at 947 and 472 cm⁻¹ in FT–IR and 429, 390, 229 and 207 cm⁻¹ in FT–Raman.

4.3 NBO and NLMO analysis

The Natural bond orbital (NBO) calculations were performed at B3LYP level using Gaussian 09 W program package. A useful feature of the NBO method is that it gives information about interactions in filled and virtual orbital spaces that could improve the analysis of intra and intermolecular interactions [28, 29]. NBO analysis provides the most accurate possible 'Natural Lewis Structure' picture of 'j' because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. The second-order Fockmatrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis. The interactions result is a loss of occupancy from the localized NBO of them idealized Lewis structure into an empty non-Lewis orbital. For each donor (*i*) and acceptor (*j*) the stabilization energy E(2) associated with the delocalization $i \rightarrow j$ is determined as

$$E(2) = \Delta E_{ij} = q_i \frac{F_{(i,j)}^2}{\varepsilon_j - \varepsilon_i}$$

 q_i is the donor orbital occupancy, ε_j , ε_i the diagonal elements, and $F_{(ij)}$ is the off diagonal NBO Fock matrix element. Furthermore, the more donating tudency from electron donors to electron acceptors is the main requirement for the greater conjugation in the investigated system. Delocalization of electron density between occupied Lewis-type (bonding or lone pair) NBO's and formally unoccupied (antibonding or Rydberg) non-Lewis NBO's correspond to a stabilizing donor–acceptor interaction. The important interactions between 'filled' (donors) Lewis-type NBOs and 'empty' (acceptors) Non-Lewis NBOs according to second order perturbation energy values, E(2) of 4MNBO were given in Table S1(Supplementary material).

The strong intramolecular hyperconjugative interaction of the σ and π electrons of C–C to anti C–C bond of the ring leads to stabilization of some part of the ring as evident from Table S1(Supplementary material). For example, the most important highest energy, related to the molecule was electron donating from $\pi^*(C_{10}-C_{15})$ to the antibonding acceptor $\pi^*(C_6-C_7)$ with stabilization energy 256.22 KJ/mol. In addition, the intra-molecular hyperconjugative interaction LP(2) O₁₆ $\rightarrow \pi^*(C_{11}-C_{12})$ and $\pi(C_{10}-C_{15}) \rightarrow \pi^*(C_{13}-C_{14})$ leading to stabilization of 25.06 and 19.36 kJ/mol.

The Natural Localized Molecular Orbital (NLMO) analysis was carried out since they show how bonding in a molecule was composed from orbitals localized on different atoms. The derivation of NLMOs from NBOs gives direct insight into the nature of the localized molecular orbital's ''delocalization tails'' [30, 31]. Table S2 (Supplementary material) shows the significant NLMO's occupancy, percentage from parent NBO and atomic hybrid contributions of 4MNBO calculated at B3LYP level using 6-311++G(d,p) basis set. The most delocalized NLMO shown in Table S2 (Supplementary material) has only 76.43% contribution from the localized $\pi(C_{10}-C_{15})$ parent NBO. The delocalization tail (22%) consists of the hybrids of C₁₄, C₁₁, C₉, C₁₃, C₈, C₇ and C₆. Similarly, the NLMO due to $\pi(C_{11}-C_{12})$ parent NBO was (16%) delocalization tail. The NLMO of second lone pairs of oxygen atom O₁₆ was the delocalized nLMO and has nearly 93% contribution from the LP(2)O₁₆ parent NBO and the delocalized tail (4%) consist of the hybrids of C₁₂ and C₁₁. Similarly, the NLMO of LP (2) O₅ have almost (~4%) delocalization tail. This delocalization can also be observed in the perturbation theory energy analysis given in Table S2 (Supplementary material).

4.4 The Natural charge analysis

The Natural atomic charges of 4MNBO obtained by Natural bond orbital analysis by B3LYP method with 6-311++G(d,p) basis set were listed in Table 3. The natural charges were shown in Fig. 4. It is an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure and other molecular properties of molecular systems [32].

The natural charge analysis of 4MNBO shows that presence of oxygen atoms were negative charge ($O_5 = -0.53850$; $O_{16} = -0.53440$). The maximum positive atomic charge was obtained for C_2 atom when compared with all other atoms, due to the attachment of negatively charged oxygen atom. The carbon $atom(C_1)$ have more negative charges whereas all the hydrogen atoms have positive charges. For the hydrogen atoms, the differences in calculated charge were relatively smaller. It was worth mentioning that the biggest value of charge was noticed for H_{18} atom.

4.5 UV–Vis spectral analysis

On the basis of a fully optimized ground-state structure, TD-B3LYP/6-311++G(d,p)have been used to determine the low-lying excited states of 4MNBO. The UV-Vis spectra analyses of 4MNBO have been investigated in water, methanol and gas phase by theoretical calculation. The experimental spectrum of the title compound in methanol was recorded with in the 200-400 nm range and shown in Fig. 5. The computed result shows that the Highest Occupied Molecular Orbital to Lowest Unoccupied Molecular Orbital transition corresponds to the λ_{max} absorption band in the UV–Vis spectrum [33, 34]. The calculated results involving the vertical excitation energy (E), oscillator strength (f) and wavelength (λ) were compared with the experimental wavelength as given in Table 4. As it can be seen from Fig. 5, experimental spectrum of 4MNBO shows three bands at 261.00, 270.40 and 318.80 nm. From the TD-DFT calculation, the most significant theoretical absorption bands were predicted at 279.21, 281.11 and 317.51 nm in methanol solution. The TD-DFT calculation predicts one electronic transition at 317.51 nm with an oscillator strength f = 0.0705, in fairly agreement with the experimentally measured narrow shoulder at 318.80 nm in methanol solution. This electronic absorption corresponds to the transition from the ground to the first excited state and was mainly described by one electron excitation from the HOMO \rightarrow LUMO.

4.6 Frontier molecular orbital's

Chemical reactivity of a molecule can be determined from the HOMO–LUMO energy gap. HOMO–LUMO energy gap plays a very important role in determining the chemical reactivity, stability of the molecule [35].

The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) were the most important orbitals in a molecule which was shown in Fig. 6 and listed in Table 5. The LUMO as an electron acceptor represent the ability to obtain an electron. The HOMO represents the ability to donate an electron [36, 37]. The HOMO–LUMO separation was a result of significant degree of intermolecular charge transfer from the electron donor groups to the electron acceptor groups through π conjugated paths. The energy gap between HOMO and LUMO has been also used to prove the bioactivity from intramolecular charge transfer (ICT). The positive and negative phases were represented in light blue and yellow color respectively. The HOMO–LUMO energy gap of 4MNBO was calculated at B3LYP level with 6–311G(d,p) and 6–311++G(d,p) basis sets as given below:

HOMO-LUMO energy gap B3LYP/6-311G(d,p) = 4.4091 eV. HOMO-LUMO energy gap B3LYP/6-311++G(d,p) = 4.3827 eV.

We focus on the HOMO and LUMO energies in order to determine interesting molecular/atomic properties and chemical quantities [38]. In simple molecular orbital theory approaches, the HOMO energy was related to the Ionization potential (I) and the LUMO energy was used to estimate the electron affinity (A) respectively by the following relations:

 $I = - E_{HOMO}$ and $A = - E_{LUMO}$.

The absolute hardness of the molecule was $(\eta) = (I-A)/2$.

The softness was the inverse of the hardness $(S) = 1/\eta$.

The chemical potential of the molecule was $(\mu) = -(I + A)/2$.

The electrophilicity index of the molecule was $(\omega) = \mu^2/2\eta$.

The electronegativity of the molecule was $(\chi) = (I+A)/2$.

The values of ionization potential, electron affinity, global hardness, global softness, chemical potential, electrophilicity and electro negativity were -5.6200, -1.2109, 2.2045, -0.4536, 3.4154, -2.6457, -3.4154 and -5.7297, -1.3470, -2.1913, -0.4563, 3.5383, 2.8566, -3.5383 eV respectively in gas phase, calculated at B3LYP level with 6–311G(d,p) and 6–311++G(d,p) basis sets respectively for the title molecule. A large HOMO–LUMO energy gap implies high stability. High stability of a molecule reflects its low reactivity toward chemical reactions in some sense. Considering the chemical hardness and large HOMO–LUMO energy gap means a hard molecule and small HOMO–LUMO energy gap means a soft molecule. We can assume that the stability of the molecule to softness with least HOMO–LUMO energy gap. In addition, a soft molecule has an easily changed electron distribution so it is correspond to more reactive site than hard molecules. Both HOMO and LUMO were mostly localized on benzene rings. The energy gap was found to be 4.3827 eV, which implies that the title molecule has high kinetic susceptibility and low chemical reactivity. The principle of hardness works in chemistry and physics but it was not physically observable. Soft systems were large and highly polarizable, while hard systems were relatively small and much less polarizable.

4.7 Molecular electrostatic potential

The molecular electrostatic potential (MESP) surface of the molecule under investigation were constructed by using B3LYP/6–311++G(d,p) method using Gauss view 5.0 program. The MESP surface provides a visual method to understand the relative polarity of a molecule. The MESP surface was plotted for molecule as shown in Fig. 7. MESP surface of a molecule was the net electrostatic effect produced by the total charge distribution (electrons and nuclei). MESP surface depicts not only the site for reactivity but also the size, shape and charge distribution of a molecule [39, 40]. The different values of the electrostatic potential at the surface were represented by different colors. The negative (red) regions were related to electrophilic reactivity and the positive (blue) ones to nucleophilic reactivity. The color scheme for the MESP surface were as follows: red for electron rich, partially negative charge; blue for electron deficient, partially positive charge; light blue for slightly electron deficient region; yellow for slightly electron rich region; green for neutral; respectively.

The color code of this surface was between in the range of 0.0393 a.u. (deepest blue) and - 0.0762 a.u. (deepest red) for the compound, where blue indicates the strongest attraction and red indicates the strongest repulsion [41, 42]. The MESP surface, the negative electrostatic potentials were shown in red color and the intensity of which was proportional to the absolute value of the potential energy and positive electrostatic potentials were shown in blue color. The calculated MESP map show the negative regions were electrophilic regions; these were mainly over the carbonyl groups. The positive regions were the nucleophilic region and these were over the hydrogen atoms of the title molecule. From these results, one can conclude that the H atoms indicate the strongest attraction and O atoms indicate the strongest repulsion.

4.8 Thermodynamic properties

The thermodynamic parameters supply helpful and extra information about the title molecule. The values of some thermodynamic parameters (such as zero-point vibrational energy, thermal energy, specific heat capacity, rotational constants and entropy) of 4MNBO by B3LYP method with 6-311G(d,p) and 6-311++G(d,p) basis sets and listed in Table 6. The ZPVE was lower in the B3LYP/6-311++G(d,p) than by B3LYP/6-311G(d,p) method. The calculated values of ZPVE of 4MNBO were 170.5820 kcal/mol and 170.3766 kJ/mol obtained by B3LYP with 6-311G(d,p) and 6-311++G(d,p) basis sets respectively. The direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments were strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. As a result of DFT/B3LYP calculations, 6-311++G(d,p) basis set predicts the dipole moment larger than 6-311G(d,p) basis set.

The temperature dependence of the thermodynamic properties heat capacity at constant volume ($C_{p,m}^{0}$), entropy (S_{m}^{0}) and enthalpy (H_{m}^{0}) for the title compound were also determined by B3LYP/6-311++G(d, p) method and were listed in Table 7. It can be observed that these thermodynamic functions were increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature [43].

The correlation equations between heat capacity, entropy, enthalpy changes and temperatures were fitted by quadratic formulas and the corresponding fitting factors (\mathbb{R}^2) for these thermodynamic properties were 0.9988, 0.9999 and 0.9994 respectively. The corresponding fitting equations were as follows and the correlations graphs were showed in Fig. 8.

$$C^{0}_{p,m} = 15.8423 + 0.96217T - 3.7099 \times 10^{-4}T^{2} \quad (R^{2} = 0.9988)$$

$$S^{0}_{m} = 268.6673 + 1.0368T - 2.2068 \times 10^{-4}T^{2} \quad (R^{2} = 0.9999)$$

$$H^{0}_{m} = -9.4030 + 0.1077T + 2.8022 \times 10^{-4}T^{2} \quad (R^{2} = 0.9994)$$

All the thermodynamic data supply helpful information for the further study on the 4MNBO. They can be used to compute the other thermodynamic energies according to relationship of thermodynamic functions and estimate the directions of chemical reactions according to the second law of thermodynamics in thermochemical field [44]. It must be noticed that all thermodynamic calculations were done in gas phase and they could not be used in solution.

Conclusion

The experimental and theoretical vibrational analysis of 4MNBO has been performed. The molecular geometry and vibrational wavenumber of the molecule in the ground state have been calculated by DFT/B3LYP with 6-311G(d,p) and 6-311++G(d,p) basis sets. On the basis of the experimental results and the PED calculations, assignments of all the fundamental vibrational frequencies were done. The computed optimized geometry values were compared with the experimental data. The observed and the calculated frequencies have been in fairly agreement. The intermolecular contacts have been interpreted by NBO and NLMO analysis. The natural atomic charge of the title molecule were determined and analyzed. The HOMO and LUMO orbital's have been visualized. The temperature dependence of thermodynamic parameters in the range of 100–1000 K have been determined and found that all thermodynamic properties increase with rise in temperature.

The UV–Vis spectrum have been measured in methanol solution and have been compared with the theoretical values in the gas phase and in methanol environment using TD–DFT/ B3LYP/6–311++G(d,p) basis set. The MESP surface showed that the most electrophilic sites were on electronegative atoms as well as the most nucleophilic sites were around the hydrogen atoms.

References

[1] S.M. Basha, G.D. Rao, C.H.M. Babu, P.B. Rao, C.H.H. Prasad, P. Praveen, International Journal of Pharmacy and Pharmaceutical Sciences. 2 (2010) 165–167.

[2] K. Kobylinska, M. Barlinska, M. Kobylinska, Journal of Pharmaceutical and Biomedical Analysis. 32 (2003) 323–328.

[3] B.N. Patel, N. Sharma, M. Sanyal, A. Prasad, P.S. Shrivastav, Biomedical Chromatography. 22 (2008) 1213–1224.

[4] M. Lahmek, A.A. Ramadan, Asian Journal of Chemistry. 20 (2008) 2969–2978.

[5] S.V. Gandhi, S.S. Ranher, P.B. Deshpande, D.K. Shah, Journal of the Brazilian Chemical Society. 22 (2011) 1068–1072.

[6] Y.S. Rao, K.P. Chowdary, R.J. Seshagiri, Indian J. Pharm Sci. 65 (2003) 206–207.

[7] K. Kobylin ska, M. Barli ska, M. Kobyli ska, J. Pharm. Biomed Anal. 32 (2003) 323–328.

- [8] P.K. Sahu, M.M. Annapurna, E-J. Chem. 6 (2009) S59–S64.
- [9] A.E. Bretnall, G.S. Clarke, J. Chromatogr A. 700 (1995)173–178.
- [10] V. Dumitrescu, V. David, A. Pavel, Rev. Chim. 52 (2001) 317–320.
- [11] P. Richter, M.1. Toral, G. Quiroz, P. Jaque, Lab. Rob. Autom. 9 (1997) 255–262.
- [12] J.A.M. Pulgarin, A.A. Molina, M.T.A. Pardo, Anal. Chim. Acta 528 (2005) 77-82.
- [13] Y.Altun, B. Dogan, S.A. Ozkan, B. Uslu, Acta Chim. Slov. 54 (2007) 287–294.

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

[15] A.D. Becke, J. Chem. Phys. 98 (1993) 5648-5652.

[16] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B37 (1998) 785-789.

[17] A. Frisch, A.B. Nielson, A.J. Holder, GAUSSVIEW User Manual, Gaussian Inc, Pittsurgh PA (2000).

[18] M.H. Jamroz, Vibrational energy Distribution Analysis VEDA 4, Warsaw, Poland (2004).

[19] P.P. Christopher, G.L. Adam, L. Meidong, M.J. Adam, Crystal Growth & amp Design. 2 (2002) 1–501.

[20] V. KrishnaKumar, N. Prabavathi, Spectrochim. Acta A 72 (2009) 738-742.

[21] R.L. Peesole, L.D. Shield, I.C. McWilliam, Modern Methods of Chemical Analysis, Wiley, New York, 1976.

[22] Y.R. Sharma, Elementary Organic Spectroscopy-Principles and Chemical Applications, S. Chande & Company Ltd., New Delhi, 1994.

[23] G. Socrates, Infrared Characteristic Group frequencies, Wiley-Interscience Publication, New York, 1980.

[24] M. Silverstein, G. Clayton Basseler, C. Morill, Spectrometric Identification of Organic Compound, Wiley, NewYork, 1981.

[25] B. Lambert, Introduction to organic spectroscopy, Macmillan Publication. New York, 1987.

[26] S. Gunasekaran, P. Arunbalaji, S. Seshadri, S. Muthu, Indian J. pure. Appl. Phys. 46 (2008) 162–168.

[27] D. Shoba, S. Periandy, M. Karabacak, S. Ramalingam, Spectrochim. Acta Part A 83 (2011) 148–146.

[28] J. Choo, S. Kim, H. Joo, Y. Kwon, J. Mol. Struct. (Theochem.) 587 (2002) 1-8.

[29] P. Govindasamy, S. Gunasekaran, G. R. Ramkumaar, Spectrochim Acta Part A 130 (2014) 621–633.

[30] A.E. Reed, P.V.R. Schleye, Inorg. Chem. 27 (1988) 3969-3987.

[31] R.J. Xavier, E. Gobinath, Spectrochim. Acta A 91 (2012) 248-255.

[32] R. John Xavier, E. Gobinath, Spectrochim. Acta Part A 97 (2012) 215–222.

[33] D. Shoba, S. Periandi, S. Boomadevi, S. Ramalingam, E. Fereyduni, Spectrochim Acta Part A. 118 (2014) 438–447.

[34] M. Govindarajan, M. Karabacak, S. Periandy, D. Tanuja, spectrochim. Acta Part A 97 (2012) 231–245.

[35] N. Choudhary, S. Bee, A. Gupta, P. Tandon, Comp. Theor. Chem. 1016 (2013) 8–21.[36] P. Govindasamy, S. Gunasekaran, S. Srinivasan, Spectrochim Acta Part A 130 (2014) 329–336.

[37] G. Gece, Corros. Sci. 50 (2008) 2981–2992.

[38] R.J. Parr, L.V. Szentpaly, S. Liu, J. Am. Chem. Soc. 121 (1999) 1922–1924.
[39] J.M. Seminario, Recent Developments and Applications of Modern Density Functional Theory, Elsevier. 4 (1996) 800–806.

[40] J.S. Murray, K. Sen, Molecular Electrostatic Potentials, Concepts and 399 Applications, Elsevier, Amsterdam, 1996.

[41] P. Politzer, J.S. Murray, Theor. Chem. Acc. 108 (2002) 134–142.
[42] F.J. Luque, J.M. Lopez, M. Orozco, Theor. Chem. Acc. 103 (2000) 343–345.

[43] J. Bevan Ott, J. Boerio-Goates, Calculations from Statistical Thermodynamics,

Academic Press, 2000.

[44] P. Govindasamy, S. Gunasekaran, J. Mol. Struct 1081 (2015) 96-109. Acctebrace





Fig. 2. Experimental and simulated FT–IR spectra of 4MNBO.

AC



Fig. 3. Experimental and simulated FT–Raman spectra of 4MNBO.



Fig. 4. Natural charge distribution in 4MNBO.



Fig. 5. Observed UV–Visible spectrum of 4MNBO.



Fig. 6. HOMO and LUMO plots of 4MNBO.



Fig. 7. Molecular electrostatic potential surface of 4MNBO.



Fig. 8. Thermodynamic properties of 4MNBO.

Table 1

Parameter	B3LYP/6–311G(d,p)	B3LYP/6–311++G(d,p)	Experimental	
Bond length (Å)				$ \land $
C_1 - C_2	1.5188	1.5177	1.5076	
C_1 - H_{18}	1.0892	1.0894		Þ
C_1 - H_{19}	1.0940	1.0936	0-	
C_1 - H_{20}	1.0950	1.0955		
C ₂ -C ₃	1.5235	1.5224	1.5092	
C ₂ -O ₅	1.2103	1.2121	1.2030	
C_3-C_4	1.5350	1.5350	1.5177	
C ₃ -H ₂₁	1.0972	1.0972		
C ₃ -H ₂₂	1.0977	1.0980		
C4-C7	1.5114	1.5119	1.4950	
C ₄ -H ₂₃	1.0922	1.0921		
C_4-H_{24}	1.0942	1.0943		
C_6-C_7	1.3761	1.3766	1.3692	
C ₆ -C ₁₅	1.4199	1.4205	1.4172	
C ₆ -H ₂₅	1.0865	1.0866		
C ₇ -C ₈	1.4235	1.4238	1.4204	
C ₈ -C ₉	1.3708	1.3717	1.3611	
C ₈ -H ₂₆	1.0860	1.0860		
C9-C10	1.4222	1.4226	1.4190	
C ₉ -H ₂₇	1.0851	1.0851		
C_{10} - C_{11}	1.4113	1.4120	1.4146	
C_{10} - C_{15}	1.4310	1.4309	1.4231	
$C_{11}-C_{12}$	1.3808	1.3806	1.3768	
C ₁₁ -H ₂₈	1.0839	1.0840		
C ₁₂ -C ₁₃	1.4173	1.4171	1.4162	
C ₁₂ -O ₁₆	1.3658	1.3675	1.3611	
C_{13} - C_{14}	1.3762	1.3771	1.3738	
C ₁₃ -H ₂₉	1.0817	1.0817		
C_{14} - C_{15}	1.4146	1.4149	1.4161	

Optimized geometrical parameters of 4MNBO.

C_{14} - H_{30}	1.0851	1.0852		
O ₁₆ -C ₁₇	1.4201	1.4209	1.4190	
C ₁₇ -H ₃₁	1.0889	1.0889		
C ₁₇ -H ₃₂	1.0959	1.0955		
C ₁₇ -H ₃₃	1.0958	1.0955		
Bond angle (°)			0	
C_2 - C_1 - H_{18}	109.6715	109.9740		
C_2 - C_1 - H_{19}	110.9622	111.3263	0-	
$C_2 - C_1 - H_{20}$	109.8774	109.2705		
H_{18} - C_1 - H_{19}	109.9729	110.1883		
H_{18} - C_1 - H_{20}	109.3140	108.9670	5	
H_{19} - C_1 - H_{20}	106.9952	107.0390		
$C_1 - C_2 - C_3$	116.3514	116.2757	116.2500	
$C_1 - C_2 - O_5$	121.6599	121.5908	121.5300	
$C_3-C_2-O_5$	121.9886	122.1326	122.2100	
$C_2-C_3-C_4$	113.8089	114.2063	113.9800	
C_2 - C_3 - H_{21}	108.4576	108.3154		
C_2 - C_3 - H_{22}	107.9012	107.5087		
C_4 - C_3 - H_{21}	111.0436	111.1581		
C_4 - C_3 - H_{22}	110.2920	110.3076		
H_{21} - C_3 - H_{22}	104.9066	104.8610		
$C_3-C_4-C_7$	112.6235	112.5892	112.8200	
C ₃ -C ₄ -H ₂₃	108.8343	108.9349		
C ₃ -C ₄ -H ₂₄	108.7968	108.8728		
C ₇ -C ₄ -H ₂₃	110.1929	110.0930		
C7-C4-H24	110.1765	110.0912		
H_{23} - C_4 - H_{24}	105.9848	106.0367		
C ₇ -C ₆ -C ₁₅	121.8695	121.8733	121.4900	
C ₇ -C ₆ -H ₂₅	119.7657	119.7852		
C ₁₅ -C ₆ -H ₂₅	118.3640	118.3406		
$C_4 - C_7 - C_6$	121.5861	121.5861	121.1000	
$C_4-C_7-C_8$	120.1106	120.1361	120.5400	
$C_{6}-C_{7}-C_{8}$	118.2958	118.2726	118.6400	
C ₇ -C ₈ -C ₉	121.5925	121.6015	121.2800	

$C_7 - C_8 - H_{26}$	118.8940	118.9608	
C9-C8-H26	119.5105	119.4342	
$C_8-C_9-C_{10}$	120.9132	120.9102	120.7200
$C_8-C_9-H_{27}$	120.2672	120.2172	
C_{10} - C_{9} - H_{27}	118.8182	118.8710	
$C_9-C_{10}-C_{11}$	122.4712	122.4391	121.6400
$C_9-C_{10}-C_{15}$	118.0617	118.0514	118.3200
C_{11} - C_{10} - C_{15}	119.4664	119.5087	119.6100
C_{10} - C_{11} - C_{12}	120.9179	120.8322	120.6500
C_{10} - C_{11} - H_{28}	120.3975	120.2701	
C_{12} - C_{11} - H_{28}	118.6846	118.8977	2
C_{11} - C_{12} - C_{13}	119.8901	119.9889	120.2600
C_{11} - C_{12} - O_{16}	116.3948	116.4555	114.1300
C_{13} - C_{12} - O_{16}	123.7151	123.5556	125.1500
C_{12} - C_{13} - C_{14}	119.9744	119.9328	120.0400
C_{12} - C_{13} - H_{29}	120.5489	120.6142	
C_{14} - C_{13} - H_{29}	119.4767	119.4530	
C_{13} - C_{14} - C_{15}	121.5867	121.5669	120.7300
C_{13} - C_{14} - H_{30}	119.4892	119.4552	
C_{15} - C_{14} - H_{30}	118.9240	118.9780	
$C_6 - C_{15} - C_{10}$	119.2661	119.2898	119.3600
$C_6-C_{15}-C_{14}$	122.5695	122.5394	121.8000
C ₁₀ -C ₁₅ -C ₁₄	118.1643	118.1705	118.6000
C ₁₂ -O ₁₆ -C ₁₇	118.9503	119.0433	117.1100
O ₁₆ -C ₁₇ -H ₃₁	105.7195	105.7397	
O ₁₆ -C ₁₇ -H ₃₂	111.7082	111.5842	
O ₁₆ -C ₁₇ -H ₃₃	111.7145	111.5825	
H_{31} - C_{17} - H_{32}	109.0974	109.1633	
H ₃₁ -C ₁₇ -H ₃₃	109.1003	109.1728	
$H_{32}-C_{17}-H_{33}$	109.3888	109.4912	

Table 2

Mode	Expe	erimental	Calcu	lated way	venumber (cm	n ⁻¹)	Vibrational band
no	wavenu	mber (cm^{-1})	B3LY	(P/	B3LY	Έ /	Assignment (% PED)
	v(IR)	u(Raman)	6–311G	(d,p) Scaled	6-311++(Un scaled	J(d,p) Scaled	
1	0(110)	3096vw	3203	3091	3204	3091	
2		3070vw	3183	3072	3182	3071	CH(100)
2	3057m	3079VW	3171	3061	3171	3060	^v CH(100)
Л	5057111		3164	3054	3164	3053	CH(03)
+ 5			3150	3040	3140	3030	$_{\rm b}$ CH(95)
5			2148	3040	2149	3039	$_{\rm U}$ CH(93)
0			2120	2020	2127	2027	$\frac{1}{2} \operatorname{CH}(93)$
/	2011		2121	2020	2122	2022	$_{\mathrm{v}}\mathrm{CH}_{3}(82)$
8	3011W		3131	3022	3132	3022	$_{v}CH_{3}(92)$
9			3089	2982	3089	2981	$_{\nu}CH_{2}(71)$
10			3086	2978	3086	2978	$_{\nu}\mathrm{CH}_{2}(53)$
11	2956s		3057	2951	3062	2954	$_{v}\mathrm{CH}_{2}(70)$
12	2936m	2932vw	3046	2940	3044	2938	$_{\nu}CH_{2}(64)$
13			3037	2931	3036	2930	$_{\nu}CH_{2}(63)$
14			3030	2924	3029	2923	$_{v}CH_{3}(51)$
15	2905m		3012	2907	3010	2905	$_{v}CH_{2}(63)$
16	2896m	2895vw	3000	2895	3003	2898	_v CH ₃ (47)
17	1705vs	1704vw	1784	1722	1780	1718	_v OC(91)
18	1610vs		1676	1617	1672	1614	υCC(27)
19		1575vw	1650	1593	1646	1589	_v CC(29)
20			1604	1548	1602	1546	_v CC(22)
21	1484m	1485vw	1541	1488	1539	1485	vCC(40)
22	1466m	1457vw	1520	1467	1517	1463	$_{\delta}$ HCC(25)
23	1452m		1505	1453	1504	1452	_δ HCH(51)
24	1441m	1442vw	1493	1441	1493	1441	₀ HCH(37)
25			1493	1441	1492	1440	$_{\delta}$ HCH(53)+ _r HCCC(13)
26			1479	1428	1477	1425	_δ HCH(29)
27			1478	1427	1476	1424	δHCH(29)
28	1415m	1411vw	1467	1416	1466	1415	_δ HCH(40)

Vibrational band assignments of 4MNBO.

29	1386s	1386m	1452	1401	1450	1399	$_{\delta}$ HCH(74)
30			1448	1397	1445	1394	_v CC(52)
31	1362s	1355w	1409	1360	1408	1359	_v CC(35)
32	1343s		1396	1347	1394	1345	$_{\upsilon}CC(20)+_{\delta}HCC(10)$
33			1389	1340	1388	1340	_δ HCH(16)
34			1382	1334	1382	1333	$_{\delta}$ HCH(21)+ $_{\tau}$ HCCC(21)
35			1374	1326	1373	1325	_δ HCH(13)
36	1262vs	1271vw	1314	1269	1315	1269	$_{\delta}$ HCC(31)+ $_{\tau}$ HCCC(31)
37			1304	1259	1302	1257	THCCC(14)
38			1299	1253	1294	1249	υOC(31)
39			1286	1241	1286	1241	$_{\delta}$ HCC(21)
40	1227vs		1269	1225	1268	1223	υ CC (31)
41	1175s	1156vw	1208	1166	1206	1164	$_{\tau}$ HCOC(41)
42	1153vs		1195	1153	1194	1152	$_{\delta}$ HCC(16)
43			1186	1145	1185	1143	$_{\delta}$ HCC(19)+ $_{\upsilon}$ OC(10)
44			1179	1138	1179	1138	$_{\delta}$ HCC(21)
45			1177	1136	1175	1134	$_{\upsilon}$ CC(10)+ $_{\delta}$ OCC(13)+ $_{\tau}$ HCCC(15)
46			1170	1130	1169	1128	$_{\upsilon}$ CC(11)+ $_{\tau}$ HCOC(15)
47			1170	1129	1166	1125	$_{\delta}$ HCH(14)+ $_{\tau}$ HCOC(37)
48	1119s		1157	1117	1157	1116	$_{\upsilon}$ CC(11)+ $_{\delta}$ HCC(16)
49		1029vw	1067	1030	1065	1028	υ OC (32)
50	1027vs		1065	1028	1064	1026	υ OC (20)
51			1061	1024	1060	1023	υCC(49)
52	947m		980	946	979	945	$_{\tau}$ CCCC(11)
53	932m		973	939	975	941	$_{\tau}$ HCCC(42)
54			956	922	952	918	$_{\tau}$ CCCC(51)
55	909w		952	919	951	918	υCC(17)
56	894s	894vw	940	907	942	909	$_{\tau}$ HCCC(11)
57			914	882	912	880	$_{\tau}$ HCCC(16)
58		865vw	904	873	902	870	_t HCCC(53)
59	844vs	832vw	879	849	880	849	_r HCCC(54)
60	815s		860	830	860	829	υCC(22)
61	798m	795vw	828	799	827	798	δ CCC(10)
62			814	785	812	784	υCC(13)

63	766w	766w	813	785	806	777	$_{\delta}$ HCC(27)
64	736w		768	741	766	739	$_{\nu}CC(14)+_{\delta}CCC(10)$
65			765	738	759	733	γ HCCC(12)
66	694m	695vw	740	714	739	714	$_{\tau}$ HCCC(23)
67	660m		702	677	701	676	$_{\delta}$ CCC(18)
68			676	652	672	649	$_{\nu}CC(16)+_{\gamma}CCCC(12)$
69	610m	613vw	626	605	625	603	_δ CCC(10)
70	574w	576vw	584	564	582	561	ν CC(13)+ $_{\delta}$ OCC(34)
71	564w		583	562	579	558	γ OCCC(18)+ γ CCCC(11)
72	525vw	525vw	539	521	538	520	$_{\nu}CC(71)+_{\delta}CCC(12)$
73	507vw	508vw	524	506	523	505	$_{\delta}$ COC(22)
74	472vw		482	465	479	462	$_{\tau}CCCC(15)+_{\gamma}CCCC(11)$
75		443vw	479	462	478	461	γ OCCC(50)
76		429vw	443	428	443	427	$_{\delta}$ CCC(10)+ $_{\tau}$ CCCC(11)
77		401vw	420	406	419	404	$_{\delta}$ CCC(16)
78		390vw	414	400	412	398	₇ CCCC(19)
79		362vw	370	358	370	357	$_{\delta}$ COC(12)
80			336	325	334	323	$_{\delta}$ COC(19)+ $_{\tau}$ COCO(19)
81		274vw	286	276	286	276	$_{\delta}$ HCH(21)+ $_{\delta}$ COC(19)+ $_{\delta}$ CCC(32)
82		229vw	258	249	251	242	$_{\tau}$ HCOC(10)+ $_{\tau}$ CCCC(10)
83		207vw	219	211	214	207	$_{\tau}CCCC(21)+_{\gamma}OCCC(12)$
84		182vw	187	181	187	180	$_{\delta}$ OCC(34)+ $_{\delta}$ COC(10)
85			182	176	180	174	$_{\delta}$ CCC(25)
86			180	173	177	171	$_{\delta}$ CCC(16)+ $_{\tau}$ OCCC(10)
87		103vs	120	116	117	113	$_{\delta}$ CCC(22)+ $_{\tau}$ COCC(14)
88			103	99	92	89	$_{\tau}$ HCCC(17)+ $_{\tau}$ CCCC(13)
89	1		71	68	73	70	$_{\tau}$ HCCC(19)+ $_{\tau}$ CCCC(19)
90			69	66	63	61	$_{\tau}$ COCC(58)
91			40	39	40	38	$_{\tau}$ CCCC(10)+ $_{\gamma}$ CCCC(12)
92			28	27	28	27	_τ CCCC(46)
93			23	23	22	21	$_{\tau}CCCC(44)$

m-medium; w-weak; s-strong; vw-very weak; vs-very strong; v-stretching; δ -bending

; γ -Out of plane bending; τ -torsion; potential energy distribution (PED);

_

Table 3

	Ç .		
Atoms	Charges (eV)	Atoms	Charges (eV)
C_1	-0.67238	H_{18}	0.22980
C_2	0.54528	H ₁₉	0.21901
C_3	-0.46405	H_{20}	0.22637
C_4	-0.40296	H_{21}	0.21942
O_5	-0.538500	H ₂₂	0.22480
C ₆	-0.15546	H ₂₃	0.21878
C_7	-0.04487	H_{24}	0.21719
C_8	-0.19812	H ₂₅	0.20085
C9	-0.17642	H ₂₆	0.20314
C_{10}	-0.04886	H_{27}	0.20513
C ₁₁	-0.21527	H_{28}	0.21894
C ₁₂	0.29794	H ₂₉	0.21368
C ₁₃	-0.28203	H ₃₀	0.20448
C_{14}	-0.14046	H ₃₁	0.20156
C ₁₅	-0.09030	H ₃₂	0.17356
O ₁₆	-0.53440	H ₃₃	0.17405
C ₁₇	-0.22989		

The Natural charge analysis of 4MNBO.

Table 4

Wavelength (nm), Oscillatory strength (f) and Energy (eV) of 4MNBO.

		Calcu	ulated with H	B3LYP/6-	-311++G	(d,p)			Exp
G	as phase			Water		Ν	lethanol		
λ_{max} (nm)	E (ev)	f	λ_{max} (nm)	E (ev)	f	λ_{max} (nm)	E (ev)	f	λ_{max} (nm)
317.14	3.9095	0.0524	317.45	3.9056	0.0707	317.51	3.9049	0.0705	318.80
286.39	4.3292	0.0029	281.14	4.4100	0.0101	281.11	4.4074	0.0094	270.40
279.79	4.4314	0.0093	279.38	4.4378	0.0049	279.21	4.4362	0.0056	261.00

Table 5

HOMO, LUMO, HOMO-LUMO energy gap and physico-chemical properties of 4MNBO.

Table 6

Calculated thermodynamic parameters of 4MNBO.

Parameter	B3LYP/6–311G(d,p)	B3LYP/6–311++G(d,p)
Zero-Point		
Vibrational Energy (kJ/mol)	170.5820	170.3766
Rotational constant (GHz)	1.7014	1.7075
	0.1574	0.1572
	0.1517	0.1514
Thermal Energy (kJ/mol)		
Total	180.7500	180.5870
Translational	0.8890	0.8890
Rotational	0.8890	0.8890
Vibrational	178.9720	178.8090
Heat capacity constant (cal/mol ⁻¹ K ⁻¹)		
Total	60.8600	61.0150
Translational	2.9810	2.9810
Rotational	2.9810	2.9810
Vibrational	54.8980	55.0530
Entropy (cal/mol $^{-1}$ K $^{-1}$)		
Total	133.9520	133.5650
Translatioanal	42.1760	42.1760
Rotational	33.3360	33.3360
Vibrational	58.4390	58.0530
Dipole moment (Debye)		
u _x	-1.8290	-1.8580
u _y	-0.6061	-0.4154
U ₇	2.4183	2.5344
L .	2 0020	a 4 60 0

Table 7

Thermodynamic properties at different temperatures at B3LYP/6–311G++(d,p) level for 4MNBO.

GRAPHICAL ABSTRACT



HIGHLIGHTS

- Spectroscopic properties were examined by UV, FT–IR and FT–Raman techniques.
- ► HOMO-LUMO energy gap were theoretically predicted.
- > NBO and NLMO analysis of the title molecule were studied.
- Molecular electrostatic potential distribution of the molecule was calculated.
- The temperature dependence of the thermodynamic properties was investigated. \triangleright